Application No: GB 9812770.7
Claims searched: 1-19

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Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.Q): C3P (PDIE)

Int Cl (Ed.6): C08F

Other: ONLINE: WPI. JAPIO, EPODOC

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
X	WO 86/06730 A1	M&T CHEMICALS See whole document and in particular page 1, line 23 to page 2, lines 5 and 25 to page 3, line 5 and examples 4 & 6.	1-10
X, E	US 4761363	M&T CHEMICALS See whole document and in particular column 2, line 57 to column 3, line 6 and examples 3 & 5.	1-10

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

c) post exposing the washed plate, totally immersed in water, to actinic or germicidal light for a duration and drying the said article.

27. A method of processing the article as in claim 26 wherein a large proportion of the uncured composition is remove by centrifugal forces achieved by fixing the plate on to a cylinder and rotating it at a high speed.

28. A method of processing the article as in claim 27 wherein the surface temperature of the plate during rotation is greater than 80 ^{0}C.

29. A method of processing the article as in claim 26 wherein the washing process is aided by brushing and or the use of ultrasonic cleaning of a frequency of between 20 and 40 kHz..

20. A method of producing a photosensitive gel article, which comprises; (a) casting the molten photosensitive liquid composition onto a flexible transparent sheet at a temperature above its pouring point, (b) spreading to the desired thickness, (c) cooling to ambient temperature, (d) covering its upper surface with a cover sheet.

21. A method of producing a photosensitive article, which comprises the injection moulding of a photosensitive composition at a temperature of between 50 ^{0}C and 160 ^{0}C into the desired shape in a mould and cooling it until it gels before its removal from the tool. The method further comprises placing a transparent polymer backing and transparent cover sheet firmly to either faces of the mould tool and holding it in position by means of a vacuum.

22. A method of producing a photosensitive gel article as in claim 20 and 21 which further comprises exposing the article to actinic light through the transparent backing sheet for a duration.

23. Methods as in claim 22 wherein each article is packaged by placing it between two rigid boards of greater than 1 mm thickness.

24. An article as in claim 20 and 21 wherein the article is not deformed by a force of a 50 kPa at 25 ^{0}C.

25. Articles as in claim 24 wherein the article is storage stable for at least 1 year at ambient temperature (25^{0}C).

26. A method of processing the article as in claim 25 which comprises;

a) exposing the article image-wise to actinic light through the cover sheet,

b) removing the cover sheet and wash away the uncured composition at ambient temperature with water,

10. A composition in accordance with any one of the preceding claims further comprises a polymerisation inhibitor.

11. A composition as in claim 10 wherein the concentration of the inhibitor is between 0.002% and 2% based on the total weight of the composition.

12. Compositions as in claim 2 and 3 wherein the number average molecular weight of the oligomer is between 5,000 an 30,000.

13. Compositions as in claim 12 wherein the oligomer is formed from a reaction between diisocyanates and polyetherdiols and or polyesterdiols.

14. A composition as in claim 13 wherein a proportion of the diols consist of blocks of polyoxyethylene of between 5 and 40% based on the total diol concentration.

15. A composition as in claim 14 wherein a proportion of the diols consist of a tri block of polyoxyethylene -polyoxyalkylene or polyester-polyoxyethylene diol of between 10 and 70% based on the total diol concentration.

16. Compositions as in claim 15 wherein the number average molecular weights of the polyoxyethylene segments of the diols are between 300 and 2000.

17. Compositions as in claim 13 where the remainder of the polyether diol, is present in a proportion of between 10 and 80% of the weight of the oligomer.

18. A composition as in claim 1 to 17 wherein the composition is liquid and free flowing at greater than 50^0C.

19. Compositions as in claim 18 wherein the composition has a viscosity of less than about 10,000 mPa.s at 100^0C.

Claims

1. A photosensitive composition and article, useful for the manufacture of a flexographic printing plate and the like, The composition comprises
   a) an ethyleneically unsaturated resin oligomer compound
   b) an ethyleneically unsaturated diluent compound
   c) a photoinitiator
   d) a gelling agent

2. A photosensitive composition according to claim 1 where the ethyleneically unsaturated resin oligomer is a urethane acrylate.

3. A photosensitive composition according to claim 1 where the ethyleneically unsaturated resin oligomer is a urethane methacrylate.

4. A photosensitive composition according to claim 1 where the ethyleneically unsaturated diluent compound is an acrylate.

5. A photosensitive composition according to claim 1 where the ethyleneically unsaturated diluent compound is an methacrylate.

6. A composition as in claim 1 wherein the total concentration of oligomer (a) is between 30 to 95 % based on the total weight of the composition.

7. A composition as in claim 1 and 2 wherein the concentration of diluent (b) is between 5 and 70% based on the total weight of the composition

8. A composition as in claims 1 to 7 wherein the concentration of photoinitiator (c) is between 0.1 and 10% based on the total weight of the composition.

9. A composition as in claims 1 to 8 wherein the concentration of the gelling agent is between 0.1 and 10% based on the total weight of the composition.

Example 6

The procedure for Example 1 was followed except that 62.5 grams of a polyester diol (Rucoflex, molecular weight of 2500 from Ruco polymer Corporation NY) was used instead of the CAPA 720 and 80 ppm dibutyl tin dilaurate were used instead of 20 ppm.

Example 7

A composition as in Example 1 was injection moulded between two water cooled metal platens of dimensions 21 centimetres by 31 centimetres. A frame by 0.2 centimetres in depth by 1 centimetre in width was placed between the platens thus creating a cavity 19 x 29 x 0.2 centimetres. A film of polyester 125 microns in thickness was fixed to one platen and a sheet of polypropylene 25 microns in thickness was fixed to the other. The temperature of the composition was 135 ^{0}C and the pressure was 150 psi. The cavity filled in approx. 10 seconds and was sufficiently gelled so that the article could be removed without damage or distortion within 30 seconds.

Comparative Example 2

A procedure as in Example 7 was conducted using a composition as in Comparative Example 1. The article distorted easily under normal handling and was damaged.

Comparative Example 1

The procedure for Example 1 was followed except that 3 grams of Aerosil R974 from Degussa were used instead of the Disorbene. This photosensitive article had a breakage strength of less than 10 kPa. Its hardness when cured with actinic light of intensity of 3 milliWatts/ cm^2 for 30 minutes on each side was Shore A 23.

Example 2

The procedure for Example 1 was followed except 1 gram of hydroxypropylcellulose was added to the mixture.

Example 3

The procedure for Example 1 was followed except 1 gram of gelatine was added to the mixture.

Example 4

The procedure for Example 1 was followed except 1 gram of Kelzan T from Monsanto was added to the mixture.

Example 5

The procedure for Example 1 was followed except that 62.5 grams of a polypropylene glycol diol with a less than 1 % mono-ol present (Pluracol HP molecular weight of 2500 from Elastogran GmbH) was used instead of the CAPA 720.

negative 6 and figure 3 shows the resulting printing plate 7 following the removal of the cover sheet and the washing/developing process.

Example 1

50 grams of a triblock copolymer of polycaprylactone -polyoxytetramethylene-polycaprylactone (molecular weight of 2000, trade name CAPA 720 from Solvay Interox Ltd. Cheshire, UK, with OH value of 56.5 mg KOH/g, an acid value of less than 0.02 mg KOH/g and a water content of 0.01%) were mixed 100 grams of a triblock, oxyethylene oxyproplylene oxyethylene copolymer (molecular weight 2000, and an oxyethylene content of greater than 30%) (Poly G 55-56, from Olin Corporation, Stamford, CT USA), 14.8 grams of toluene diisocyanate (Lupranat T80A from Elastogran GmbH) and 20 ppm of dibutyltin dilaurate from Aldrich Chemical Company, Poole, Dorset, UK. This mixture was reacted for 90 minutes at 65°C. 22.5 grams of polypropylene glycol mono methacrylate (PPM5S low inhibitor from International Speciality Chemicals Limited, Southampton, UK) were added to the reaction and the mixture was further reacted at 80°C until practically all of the isocyanate was consumed.

38 grams of this oligomer were mixer with 5 grams of laurylmethacrylate, 5 grams of polypropyleneglycol monomethacrylate, 1 gram of triethylene glycol dimethacrylate, 1 gram of trimethylolpropane trimethacrylate, 0.2 grams of dimethoxy-2-phenylacetophenone, 0.02 grams 2,6 Di-tert-butyl-4-methylphenol (Topanol from ICI plc) and 1 gram of dibenzylidenemonosorbitolacetal (Disorbene from Roquette of Turnbridge Wells, Kent, UK). The mixture, while stirring, was heated to 130 °C. The molten mixture was stirred until it became clear and air was removed by centrifugation. A 7 millimetre layer was cast in a tray and allowed to cool and gel over a period of 24 hours. This photosensitive article had a breakage strength of 130 kPa. Its hardness when cured with actinic light of intensity of 3 milliWatts/ cm^2 for 30 minutes on each side was Shore A 25.

coated with an adhesion enhancing primer film. Preferably the thickness of the photosensitive layer is between 0.5 to 10 millimetres. For example a thickness of about 7 millimetres is preferred for corrugated board printing while certain book printing plates used thickness of less than 1mm. Optionally the photosensitive article is back exposed, prior to transportation, so that a layer of polymer is firmly adhered to the backing polyester sheet. Preferably the photosensitive article is packaged for transportation between two rigid boards of thickness greater than 1 millimetre preferably greater than 2 millimetres.

Placing a negative film against the polypropylene cover sheet side and exposing it to actinic light for a duration processes the photosensitive article. Unhardened resin is removed on a small scale process by washing it in an aqueous solution using a hand brush, while on a larger scale this process may be semi-automated as described in WO 96/18932. In an alternative and particularly simple embodiment it may be washed by placing the article on a cylinder, in a tank, and rotating the cylinder at a high speed at a temperature of greater than 80 ^{0}C such that the centrifugal force removes most of the uncured resin. This process allows for the recovery and or disposal of a substantial proportion of the uncured photosensitive resin. The remainder of the uncured resin is washed away using an aqueous solution. Preferably an ultrasonic cleaning tank with a frequency of about 20 to 40 kHz. can be used for this cleaning process. The washed plate is post hardened by immersing it in water and exposing it to a further duration of irradiation, preferably with a germicidal light. When dried a printing plate in accordance with the invention is produced and is ready to run on a print machine.

Preferred embodiments of the present invention will now be described in greater detail by reference to the following drawings, examples and comparatives examples. In figure 1, there is a cross-section of the photosensitive article. 1 is a layer of cover sheet attached to the photosensitive composition 2 and surrounded by a frame or spacer 3 with the back sheet 4 fixed to the opposite side. Figure 2 illustrates part of the development process. A canopy containing a bank of actinic lights 5 emits radiation through the transparent parts of the photographic

The photosensitive composition may include a photoinitiator synergists, colouring agents, opacifiers or absorbers of actinic light, adhesion promoters, slip agents, odour masks, wetting agents, and additional polymerisation inhibitors or stabilisers to the free radical inhibitors already contained in commercially available methacrylate or acrylate monomer diluents (b). Some of these types of additives are well known to those skilled in the art.

The photosensitive article may be produced in a continuous production process in accordance with EP 0640 878 A1 to W R Grace & Co Connecticut.

More preferably the photosensitive article is produced in a batch process by casting the molten composition described above, on to a transparent polyester film or the like and placing a transparent cover sheet on to the opposite side of the photosensitive article on cooling. A exemplary cover sheet material is polypropylene.

Even more preferably still a process of injection moulding it to the required shape produces the photosensitive article. Exemplary methods for the injection moulding are by a modification of the "lost wax process" or "investment casting process" of the injection moulding of wax. Exemplary machines for this purpose are the Epic, Bryant and Eltamby available from Eltamby Ltd. in Slough, Middlesex, UK, Shell-O-Matic available from Mayo Engineering, St Neots Cambs., UK, Mueller Phipps and Tempcraft from USA and Canada. In this embodiment, the polyester backing sheet and polypropylene cover sheet are "in mould applied. " By this we mean, a process similar to "in mould labelling" of injection blow moulded bottles. Both films are held firmly on opposite sides of the tool by vacuum. A frame or "chase" may also be inserted prior to the injection of the molten composition. This frame may remain with the moulded article. A gear or piston pump is preferred as a means of delivering the molten photosensitive composition to the mould tool. The polyester film is preferably

The gelling agent (d) used to create a photosensitive article includes the following but without limitation: 12 hydroxystearic acid, acyl amino acid amine salts, polysaccharides and substituted polysaccharides, condensates of benzaldehyde and polyols. The preferred criteria for the selection of the gelling agent (d) are: be soluble in the photosensitive composition at less than about 130 ^{0}C, more preferably less than 120 ^{0}C and form a gel state on cooling and remain gel-like on reheating from ambient to at least 50 ^{0}C; it must undergo reverse liquid to gel states on heating and cooling; it must impart gel properties such that it is not deformed by a force of 50 kPa and have an elasticity of greater than 1 %; it must form a substantially transparent composition to actinic light in the gel state and it must be stable in storage. By this we mean it must not decompose such that the photosensitive gel looses its gel property for a period of at least one-year preferably greater than 2 years. The concentration of the gelling agent in the composition is between 0.1% and 10 % by weight based on the total composition weight. More preferably it is between 1% and 5%. The concentration of gelling agent depends upon the type. Should the concentration of the gelling agent be too low the article will have insufficient gel-like properties and could easily damaged during transportation, while should the concentration be too high a proportion will not dissolve in the composition and the resultant article will be opaque or partially opaque to actinic light and the printing plate produces from this composition will be difficult to form. Certain polymers and inorganic fillers may be used to enhance the elasticity and the resistance of the photosensitive article to breakage or deformation. Exemplary polymers for this purpose are: hydroxypropylcellulose, polysaccharides such as Kelzan T from Monsanto, gelatine and low molecular weight polyvinylbutyral. Exemplary fillers are fumed silica both hydrophilic and hydrophobic. Gelling agents for resin compositions, composed of hydrophobic fumed silica, such as, R974, R972, and R812 (Aerosil is a trade mark of Degussa) at low levels of incorporation do impart gelling properties. However, even with high concentrations of these gelling agents, these compositions creep and flow under low stress. These types of inorganic gelling agents when used alone are not included in the invention.

accordance with this invention. Exemplary diluents are mono di and multi ethyleneically functional esters of acrylic or methacrylic acid and alcohol or polyols. Included and without limitation are: 2 ethylhexyl methacrylate or acrylate, laurylmethacrylate or acrylate, alkyl and hydroalkyl methacrylate or acrylate of about 8 to 20 carbon atoms, benzylmethacrylate or acrylate, isobornylmethacrylate or acrylate, trimethylcyclohexylmethacrylate or acrylate, tertiarybutyl cyclohexylmethacrylate or acrylate, phenoxyethyl methacrylate or acrylate, monoethylene, di, tri and tetraethylene glycol dimethacrylate or acrylate, hexanediol dimethacrylate or acrylate, trimethylolpropane trimethacrylate or acrylate, mono and di pentraerytritol tetra and multi methacrylate or acrylate, ethoxylated trimethylolpropane trimethacrylate or acrylate, ethoxylated di pentraerytritol tetra and multi methacrylate or acrylate, ethoxylated bisphenyl A dimethacrylate or acrylate.

Preferably the photoinitiator (c) is added to (a) and (b) in concentrations of between about 0.01% to 10% by weight of the total composition. The concentration depends upon the type of photoinitiator, the thickness of the printing plate and the wavelength of the light source used. Exemplary photoinitiators are acyl and bisacyl phosphine oxide, benzoin methy, proply and butyl ether, acetophenone derivatives such as chloroacetophenone, diethoxy acetophenone, dimethoxy 2 phenyl acetophenone and the like, camphorquinone, naphthaquinone, 2- Chlorothioxanethone, 1- hydroxycyclohexyl phenyl ketone, benzoylbenzoate, Michler's ketone, thioxanone, benzophenone, titanacene and the like. The preferred criteria for the selection of photoinitiatiors include but without limitation are cost, reactivity to light of different wavelengths, compatibility and stability with the composition, odour, colour, stability to light, toxicity and combinations of these attributes. Preferably the photinitiators may be used on their own or in combination with others or in combination with amine or amine methacrylate or acrylate synergists.

Preferably the diisocyanate is selected from the following without limitation: methylene diphenyldiisocyanate, either toluene 2,4 and 2,6 diisocyanate or mixtures of these isomers, xylene diisocyanate, naphylene diisocyanate, hexamethylene diisocyanate, cyclohexane diisocyanate, isophorone diisocyanate and the like. Preferably the ratio of diisocyanate to diol is between 10 : 9 and 3 : 2.

In a preferred embodiment the urethane methacrylate or acrylate oligomer is formed by first reacting the diols with the diisocyanate in the presence of a catalyst at about 65 ^{0}C, for about one and a half hours, or until a substantial proportion of the terminal hydroxyl groups of the diols are consumed. Exemplary catalysts are alkyl tin compounds such as dibutyltin dilaurate and stannous octoate. Typically, these catalysts are effective in a concentration of about 20-ppm, based on the total weight of the composition. Upon consumption of the hydroxy groups of the diol, the oligomer is capped with a hydroxy functional methacrylate or acrylate at a temperature of about 80 ^{0}C until substantially all of the diisocyanate has reacted or consumed.

Exemplary hydroxy functional methacrylate or acrylates are hydroxypropyl acrylate, hydroxypropyl methacrylate, hydroxyethyl acrylate, hydroxyethy methacrylate, polypropylene glycol mono acrylate or methyacrylate and the like.

Preferably the diluent monomer (b) should be selected from stabilised mono and multifunctional methacrylate or acrylate monomer. Preferably the ratio of monofunctional to multifunctional monomer should be such that the hardness of the printing plate may be regulated. The greater the proportion of multifunctional monomer the harder the eventual printing plate will be. The preferred concentration of diluent (b) is such that when mixed with (a) a viscosity of between about 10,000 and 400,000 mPa.s at 25^{0} C is achieved. A concentration between 5 and 70% based on the total weight of the composition is preferable in

A fourth aspect of the invention is a method for printing a substrate involving the transfer of ink to a substrate using a printing plate as described above.

A further aspect of the invention is an article printed with a printing plate prepared in accordance with this invention.

The photosensitive resin in accordance with the first aspect of the invention comprises typically a methacrylate or acrylated urethane oligomer, an ethyleneically unsaturated diluent compound, a photoinitiator , and a gelling agent. The urethane methacrylate or acrylate oligomer is formed by reacting polydiol with a diisocyanate and a methacrylate or acrylate containing a hydroxy functional group. Preferably the polydiol may be selected from polyether diols which include, polyethylene oxide diol, polypropylene oxide diol, polybutylene oxide diol, polyoxytetramethylene glycol, and copolyether diol of the above polyether diols. It may also be a polyesterdiol such as propylene glycol adipic acid polyester diol or polycaprolactone diol. Preferably the diols are a mixture of; (i) polyoxyethylene and polyoxypylene either block or random copolymer diols of between about 500 and 5000 in number average molecular weight and; (ii) one or more of a polyoxypropylene, polyoxytetramethylene, polyoxybutylene, polyester or polycaprylactone diols of number average molecular weight of between about 500 to 5000. The proportions of (i) and (ii) and the diisocyanate and methacrylate or acrylate are such that a number average molecular weight of between about 5,000 and 50,000 for the oligomer is obtained. More preferably the number average molecular weight of oligomer should be between about 5000 and 30,000.

Preferably the polyether diol (i) is a block polyoxyethylene and polyoxypropylene diol where the proportion of oxyethylene to oxypropylene is between about 1 : 1 and 1 : 5 respectively. In an alternative embodiment, should a diluent monomer (b) with surfactant properties be used, then the proportion of polyoxyethylene may be much lower or even reduced to zero.

oligomer or diluent monomers. Ethyleneically unsaturated urethane oligomers based on polyesters such as hexane diol-adipic acid polyester resin are solid at room temperature and molten and free flowing at about 100 ^{0}C. These are included in this alternative embodiment of the invention. The preferred criteria for the selection of a gelling agent are:

i. It must be substantially soluble in the photosensitive composition at less than about 130 ^{0}C and solidify to a gel state on cooling and remain a gel when reheated to at least about 50 ^{0}C.
ii. It must undergo reverse liquid to gel states on heating and cooling.
iii. It must impart gel properties such that the photosensitive article is not deformed by a force of less than 50 kPa at about 25 ^{0}C.
iv. It must form a substantially transparent article to actinic light.

A second aspect of the invention is a photosensitive article used to prepare a printing plate, where the photosensitive article comprises a layer of photopolymer of the inventive composition coated on to a transparent polyester or other suitable support material and covered with a transparent and substantially non adherent cover material. In an alternative embodiment the transparent cover sheet may be water dispersible or soluble. Ploy vinylalcohols and polyhydroxypropyl cellulose polymers, without limitation, are exemplary polymers in this embodiment.

A third aspect of the invention is a method for the production and processing of a photosensitive article utilising the inventive composition described above. The process includes the formulation of the photosensitive gel, its casting onto a suitable support layer, the subjection of photosensitive gel to back exposure through the transparent support (commonly referred to as the backing sheet), the method of subsequent storage, modes of packaging and transporting before the image-wise exposure to actinic light and the eventual further process of developing the polymerised composition to form a printing plate.

acrylates to each other, as is known to those skilled the art, may be selected so as to regulate the hardness and flexibility of the printing plate, while their proportion in the composition may be used to regulate viscosity. In an alternative embodiment it is preferred that these diluent monomers may also have surfactant properties.

Preferably the photoinitiator (c) used in the present invention are the free radical generators, either the hydrogen abstraction or molecular cleavage type. They are present in the composition in a concentration of about 0.01 to 10% by weight based on the total weight of the composition.

The gelling agent (d), which is incorporated in (a) and (b) by both heating and mixing, imparts gelling properties on cooling. Preferably it must be substantially soluble in (a) and (b) in the molten state. Should a proportion of the gelling agent not dissolve, the composition will loose its transparency to actinic light, resulting in a deterioration in its development properties. Preferably it also must not be present in a concentration so as the mechanical, physical and chemical properties are materially compromised. Preferably the concentration and selection of the gelling agent should be such that the photosensitive article can withstand a compressive force of greater than 50 kPa. and preferably greater than 500 kPa at ambient temperature. It is desirable that the viscosities of the composition when molten should be sufficiently low so as it will flow readily and is readily self-levelling. A viscosity of less than about 10,000 mPa.s at 100 ^{0}C is preferable in accordance with the present invention. Preferably the gelling agent must not adversely effect other properties, especially, the water developablility, or as it is more commonly referred to, as the water washability. Suitable gelling agents include but are not limited to are: polyethlyene glycol (molecular weight 3,000 to 10,000), stearic acid esters, hydroxy stearic acid, polysaccharides and acylamino acid-amine salts condensation products of benzaldehyde and polyol, such as pentaeythritol, mannitol, xylitol, sorbitol and the like. In an alternative embodiment the gelling agent may preferably be co-reacted with the base

The present inventor, flying in the face of the prior art, has surprisingly and unexpectedly found compositions and methods which overcomes these drawbacks.

In a first aspect, the present invention provides a photosensitive resin composition comprising:

a) an ethyleneically unsaturated resin oligomer compound

b) an ethyleneically unsaturated diluent compound

c) a photoinitiator

d) a gelling agent

The resin compound (a) is typically the reaction product of either random or block polyoxyethylene, polyoxypropylene, polyoxybutylene diols, polyester diols and the like with diisocyanates and capped with hydroxyl functional methacrylate or acrylate. The number average molecular weight of (a) is between about 5000 and 50,000. Preferably the proportion of polyethylene oxide, polypropylene oxide, polybuthylene oxide and other polyols such as polyoxytetramethylene glycol, polyester diol including polycaprolactone diol and the like, and their combination with, and the selection of a suitable diluent (b), must be such that the composition be water developable, whilst the resulting printing plate is substantially resistant to swelling by water based inks. Typically block polyethylene oxide segments are present in a concentration of greater 5% and less than 40% in the oligomer. It is also appreciated that, in an alternative embodiment, the polyethylene oxide proportion may be reduced to zero, should a diluent with substantial emulsification properties be used. It is preferred that the selection of the other diols in (a) and their proportions should be such that, when reacted with the diisocyanate, they impart the greatest strength, the appropriate flexibility and yield a oligomer that is substantially transparent to actinic light and in combination with the diluent (b) be soluble and also be substantially transparent. Preferably the diluent (b) is a mixture low molecular weight mono and or multifunctional methacrylate or acrylate monomers. It is also preferred that the proportions of each of the mono or multifunctional methacrylate or

and method for handling photosensitive liquids is disclosed in WO 95/33613 to Galimberti. Whilst these process represents an advancement of the art, there are also a number of difficulties with these types of packages. Some of these are:

a) there is an absence of an integral reinforcing backing sheet
b) they are easily damaged during transportation
c) they are cumbersome to use for large sizes of plates while for small sizes they are wasteful

Therefore, the production of flexographic printing plates using either liquid or sheet photosensitive compositions is not entirely satisfactory. Accordingly, the art of producing flexographic printing plates still searches for a photopolymerisable composition and methods, which avoid the problems described above.

It is the first object of the invention to provide a photopolymerisable composition which avoids the problems in the art of flexographic plate making and the like, described above.

It is the second object of the invention to provide a photosensitive article made from such a composition, which is developable by water and is suitable for use with aqueous based inks.

It is the third object of the invention to provide a method for the production of such a photosensitive article and a method of processing this article into a printing plate.

It is the fourth object of the invention to provide a method for printing a substrate, which utilises a printing plate, described above.

substantially resistant to the solvent contained in the ink, which, for flexographic printing, is typically water and or alcohol based, and it must be tough and resilient so that it is not easily damaged in use. It must also be non-tacky or have a low infinity to pick up loose particles of paper or board fibres from the substrate so that the plate does not require frequent cleaning in use.

WO 94/ 22057 to Napp Systems Inc. teaches us a process for the production of a printing plate using a solid photosensitive water developable sheet. We have found that, while developable with water and substantially resistant to swelling or distortion by aqueous based inks, this photosensitive sheet is difficult to develop with water alone, requiring either washing for a long duration of time or requiring scraping action with a stiff bristles in order to remove to undeveloped portions of the plate. There is, furthermore, a danger, particularly with a plate bearing a fine image, that this type of plate may be damaged during the development process

EP 0 453 307A2 to W R Grace & Co (Connecticut) teaches us about a photocurable sol/gel suitable as a printing plate, which undergoes reversible sol/gel on heating and cooling. These compositions comprise polymers with moieties of isotactic and syntactic polymethyl methacrylate, dissolved in photopolymerizable ethylenically unsaturated compounds, and may also include "oil gelating agents". Plates made from such compositions are hard and inflexible and are not suitable for flexographic printing of the type used for printing compressible fibrous paper substrates such as corrugated board or multiwalled paper bags and the like.

Other workers have devised a "pouch" system for a photosensitive liquid in order to overcome some of the undesirable aspects of handling such fluids. The method involves placing a transparent sachet or pouch containing a liquid photosensitive composition between transparent plates and imagewise exposing the sachet to light by methods described above. Following exposure, the plastic sachet material is removed and uncured resin is washed away. Another device

soda, and others a process of vigorous brushing and scraping in an aqueous solution, which is not only cumbersome but requires great skill so as not to damage the plate. Another drawback with some aqueous developable photosensitive sheets is that plates made from these sheets swell and is deformed when used with aqueous based inks.

Flexographic printing plates made from liquid resin compositions offer the advantage of being water developable yet resistant to substantial swelling by aqueous based ink. Producers of these compositions claim a further positive attribute. A substantial proportion of the uncured liquid can be recovered and reused. One method for the recovery of the uncured liquid, following image-wise exposure to actinic light, is achieved by suspending the plate vertically and blowing off the uncured liquid with a jet of hot air. This liquid is recovered and reused. While these processes involving photosensitive liquid compositions are more economical for short print run with aqueous based inks, they have a tendency to be tacky and some types are quickly contaminated by particles of fibres from the printing substrate. This causes a deterioration in print quality. A further drawback of these liquid photosensitive compositions and processes is that a proportion of the recovered liquid is partially polymerised or cured and the incorporation of this recovered liquid contributes to the inherent tackiness of plates. While the art of making good plates from liquid photosensitive compositions involves the use of special machinery and great skill, the plates produced using recycled resin are of variable quality and the quality deteriorates in proportion to the amount of recycled material used. In this way the plate maker is burdened with the extra responsibility of trying to controlling these undesirable and cumbersome processes. These drawbacks out weigh the economic advantages achieved by the recovery of unexposed liquid. WO 96/ 18932 to Hercules Inc. is a recent example of such compositions and processes.

The desirable chemical and mechanical properties required of a flexographic printing plate and the like is that it be flexible and elastic, it should be

acid etching of metals coated with an acid resistant polymer image or by pressing this master plate into a matrix board at elevated temperatures. Matrix boards used in the printing industry are, typically, solid thermosetable resins containing air voids.

Another method used in the process of making a printing plate is by means of a solid resin sheet composition. A layer of the photosensitive material is image-wise exposed to ultraviolet light (commonly referred to as actinic light) on one side for a duration. The unexposed portions are removed with water or solvents. Mechanical brushing is frequently used to aid the development process. Aqueous developers are preferred to organic solvent developers due to the Health and Safety, environmental and economic considerations with such organic fluids. In the case of WO 94 22057, these plates require vigorous scraping in order to satisfactorily remove uncured solid resin. Once developed the plates are post hardened by further irradiation to improve their mechanical properties.

Yet another method for the production of flexographic printing plates and the like involves the use of a photosensitive liquid composition. The process involves, as for the sheet photosensitive composition, image-wise exposure of the layer of liquid composition to actinic light. Water and surfactant alone are required to remove the unexposed and uncured composition.

All of the aforementioned processes for the production of printing plates have both positive and negative attributes. Rubber printing plates made by laser engraving or vulcanisation in a mould, whilst durable, are expensive, particularly for short run prints.

Plates made from sheet photosensitive compositions are less expensive than rubber, for short print runs, but the processes involve the use of organic solvents, which are not desirable due to environmental considerations. Other photosensitive sheet processes use aggressive chemical reagents, such as caustic

Improvements in compositions, moulding, articles and methods for printing and marking

The present invention relates to a photocurable resin composition used for making a mould or printing plate developable by water. It also relates to a photosensitive article made from this composition, a method of production and processing of this article and to a method of moulding, printing or marking.

In the case of flexographic printing, ink is transferred to a substrate from an ink reservoir by means of a printing plate. The surface of the printing plate is of a shape which is the mirror image of the printing, so that, when printed this image is reversed. These plates are mounted on cylinders and these cylinders rotate between other cylinders wetted with ink (anilox rollers). Ink is transferred from the anilox roller on to the surface of the plate and from the surface of the plate on to the substrate. In the case of flexographic printing, substrates are typically paper.

In the art of marking devices, such as rubber stamps, the printing plate, with image in reverse, is fixed to a mount and printing is achieved by manually depressing the mount onto the surface of an inkpad. In so doing, a thin layer of ink is collected on the surface of the printing plate, which is subsequently transferred on to a substrate by pressing the mount against a substrate.

Since printing plates may be used as moulds, for the purpose of reproducing an image or a mirror image, all reference hereafter to printing plates may also include moulds as well.

A variety of methods and compositions are employed to make these printing plates. Rubber plates are made either from laser engraving of already vulcanised rubber or by vulcanising a rubber composition, in a pre-shaped mould using a vulcanising press. One method of producing moulds for this purpose is by the

Figure 1

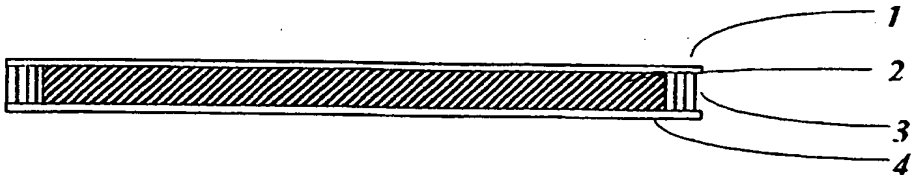

Figure 2

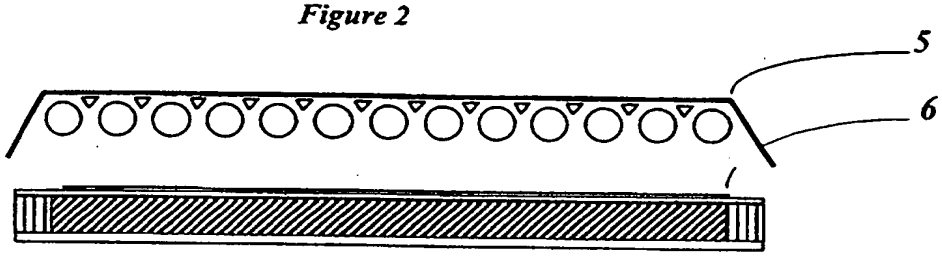

Figure 3

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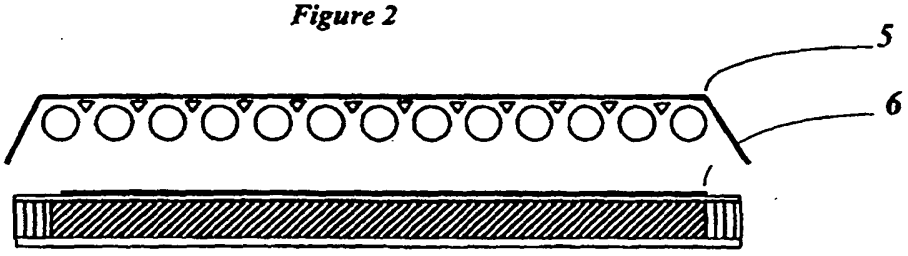
(54) Abstract Title
Photocurable resin composition

(57) A photosensitive composition comprising (a) an ethyleneically unsaturated resin oligomer compound, (b) an ethyleneically unsaturated diluent compound, (c) a photoinitiator and (d) a gelling agent. The invention is useful for printing, moulding and marking. For preference, compound (a) is a urethane (meth)acrylate and compound (b) is also preferably a (meth)acrylate.

Figure 2



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